Structures and Spectroscopic Properties of Metallocorrole Nanoparticles

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Supporting Information

Syntheses. Al-tpfc[1], Ga-tpfc[2], and tris-pentafluorophenyl corrole (H_3-tpfc)[3] were prepared using literature procedures. Insertion of a gold atom into tpfc has been particularly challenging, with the highest-yielding route utilizing excess gold(III) acetate in pyridine solvent.[4] However, with a maximum Au-tpfc yield of ~12%, along with decomposition of non-metallated tpfc (plus the need for excessive gold precursor), this final step to product was inefficient. We improved the Au-tpfc synthesis, as follows: 393 mg H_3-tpfc (0.49 mmol) were dissolved in 40 mL dichloromethane (in a dry flask). The flask was sealed with a septum and purged with inert gas. Separately, in a dry flask, 219 mg $AuCl_3$•DMS (0.60 mmol) were dissolved in 20 mL

dichloromethane. To the vigorously stirring corrole solution we added (by syringe) 1.5 mL of 1.0 M potassium *tert*-butoxide in THF (1.5 mmol) followed immediately by the $AuCl_3$•DMS solution. The solution turned green followed by red, and a precipitate formed. After 5 min, ~40 mL of silica gel were added to the reaction mixture, and the solvent was removed under reduced pressure. This was added on top of a silica filter column composed of 100 mL of silica gel, using 4:1 hexanes/dichloromethane as eluent. A red compound eluted first, and elution continued until the red faded and the eluent became green. The solvent was removed under reduced pressure to afford a brown solid. The product mixture was purified by silica gel column chromatography (1" x 12") using 4:1 hexanes/dichloromethane, and fractions were obtained. Those containing the pure product were combined and the solvent removed under reduced pressure to yield a purple/red solid that was subsequently washed with deoxygenated petroleum ether. Yield: 43%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (d, J = 4.9, 2H), 9.00 (d, J = 4.9, 2H), 8.88 (d, J = 4.9, 2H), 8.83 (d, J = 4.9, 2H). ^{19}F NMR (300 MHz, $CDCl_3$) δ -137.0 (m, 6F), -152.1 (m, 3F), -161.4 (m, 6F). Data collected in chloroform solutions using a 300 MHz Varian instrument was reported as ppm downfield of TMS (as internal standard). MALDI-TOF (*m/z*): M+ calcd for $C_{37}H_8AuF_{15}N_4$, 990.02; found, 990.05. Mass spectrometry was performed using a Bruker Autoflex MALDI-TOF instrument using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix. *Tert*-butoxide (1.0 M in THF) was obtained from Aldrich. Silica gel (F60) was obtained from Silicycle. HPLC-grade dichloromethane was stored over a drying agent.

XRD Refinement Details. A Au-tpfc crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (100K) X-ray data were collected with a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and

1 mA (Mo K_α = 0.71073 Å; PHOTON 100 CMOS detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. Au-tpfc crystallizes in the tetragonal space group $I4_1/a$ with the asymmetric unit containing one and a half (on a two-fold axis) molecules along with solvent (chloroform and pentane) disordered over one site. The molecular structure is shown in Figure S1. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} value of the bonded atom.

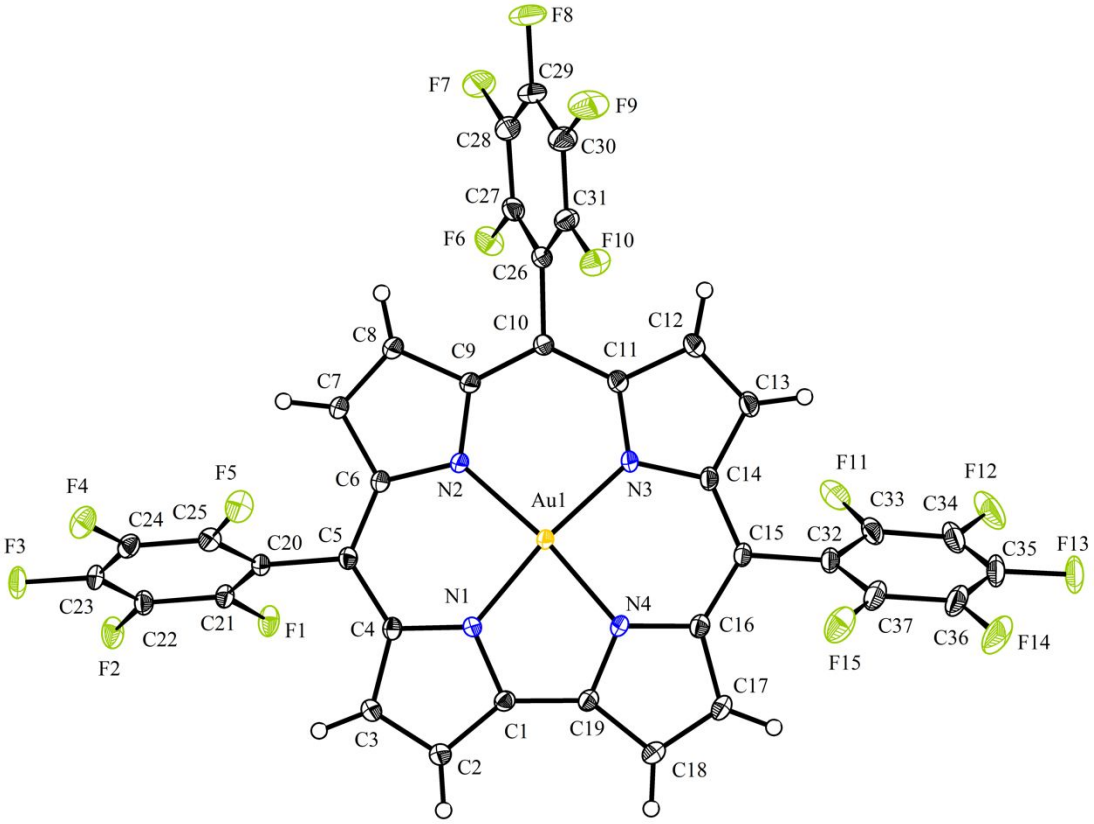


Figure S1. Displacement ellipsoid view of the Au-tpfc molecular structure. Crystallographic data (CCDC 1914233) can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/structures.

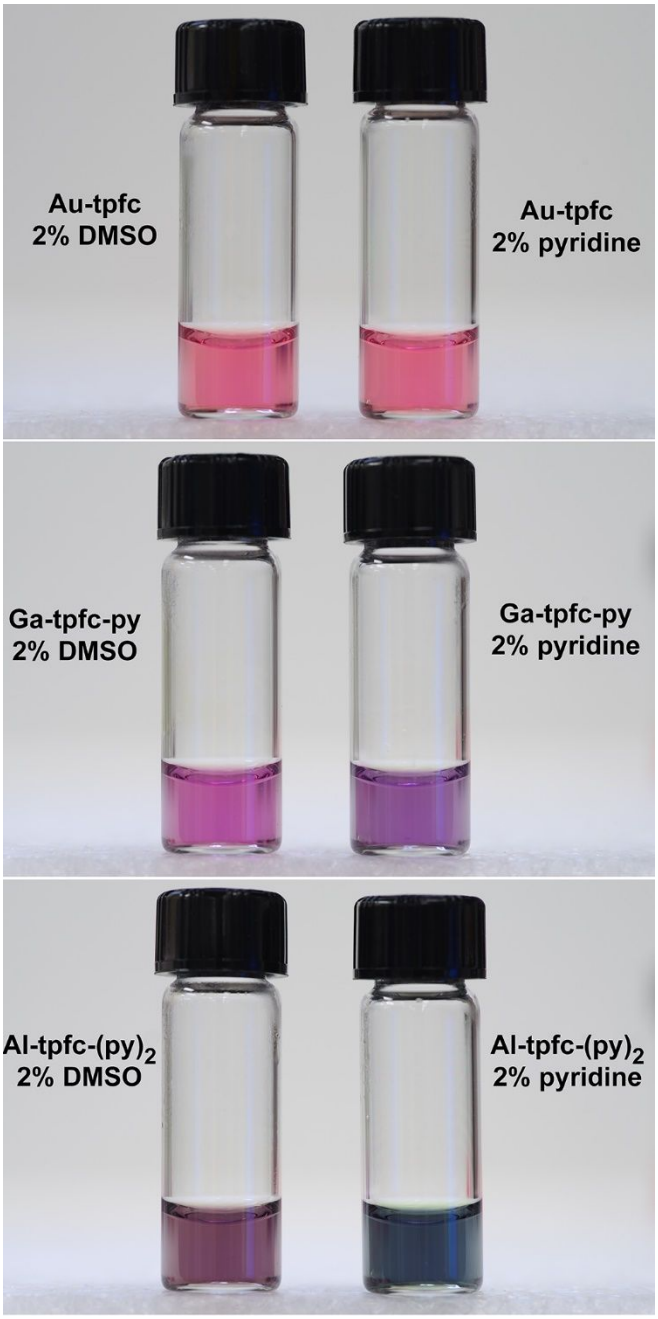


Figure S2. Freshly prepared Au-tpfc, Ga-tpfc-py, and Al-tpfc-$(py)_2$ NPs samples in 2% DMSO/water (left) and in 2% pyridine/water (right). The samples appeared stable over a 1-month.

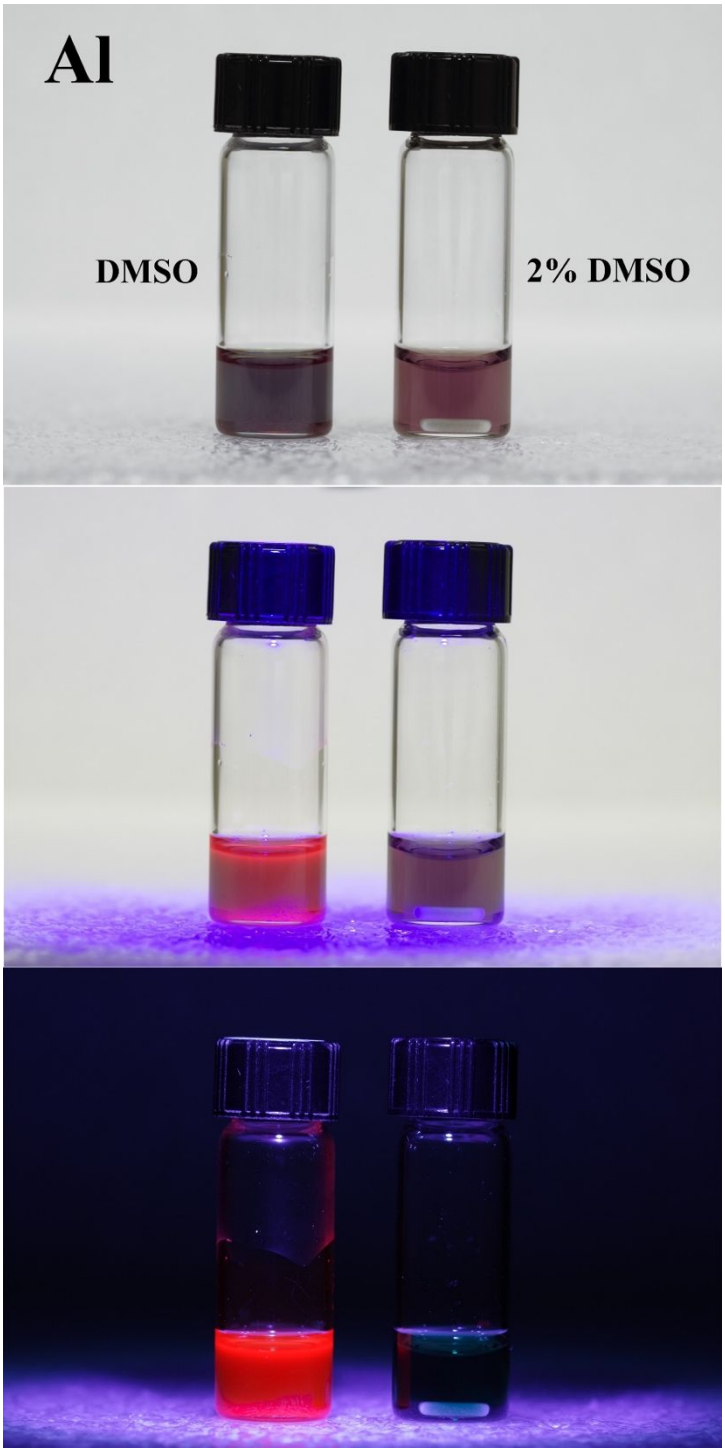


Figure S3. Freshly prepared solution of Al-tpfc in pure DMSO (top, left) and colloidal Al-tpfc in 2% DMSO/water (top, right). Both samples contain the same amount of corrole monomers. No sign of precipitation was observed for the colloidal sample. The middle panel shows the samples

illuminated with UV light under fluorescent ambient lighting. The bottom panel shows the samples only illuminated with a UV lamp. Note the quenched emission of aggregated Al-tpfc.

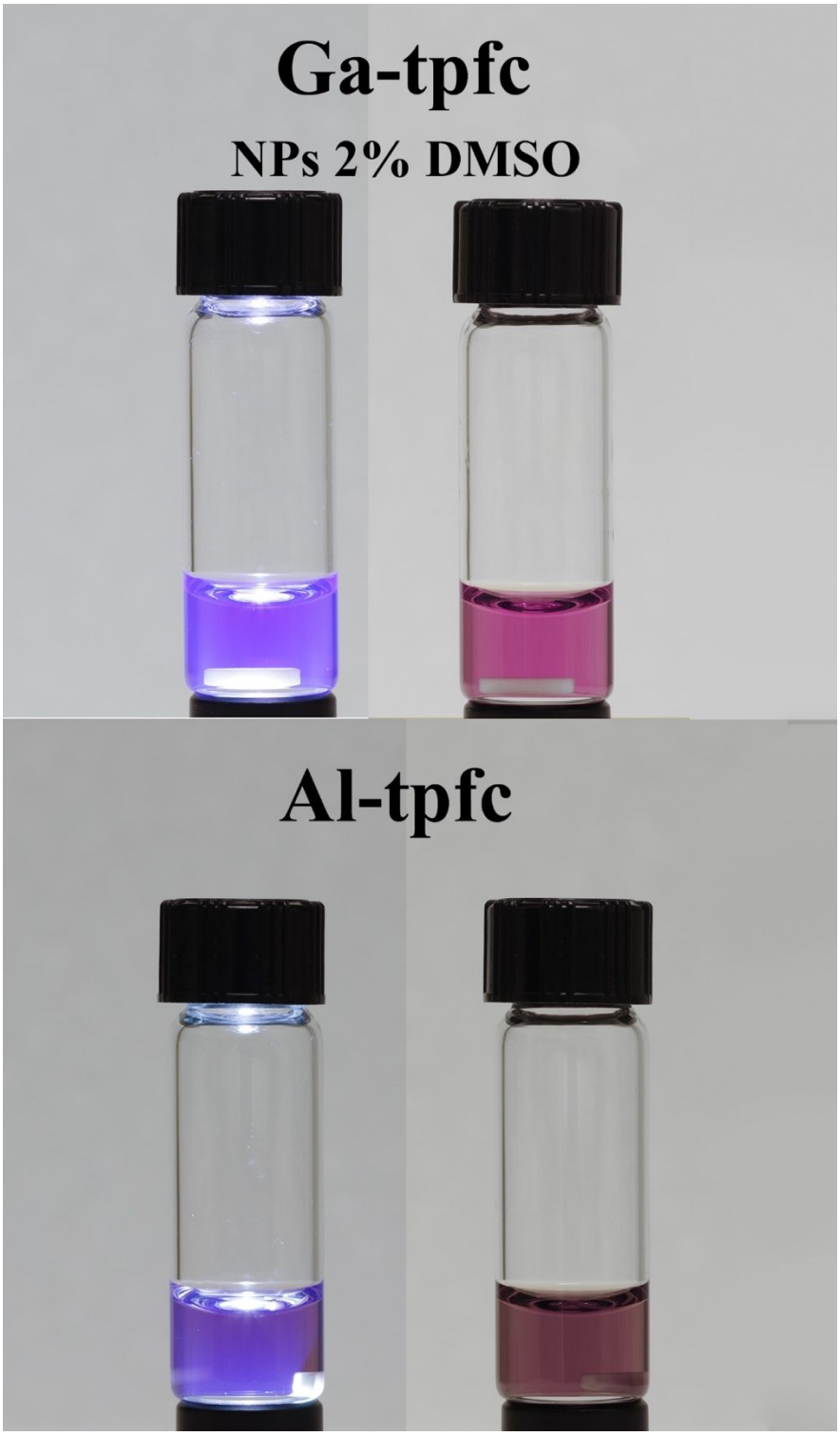
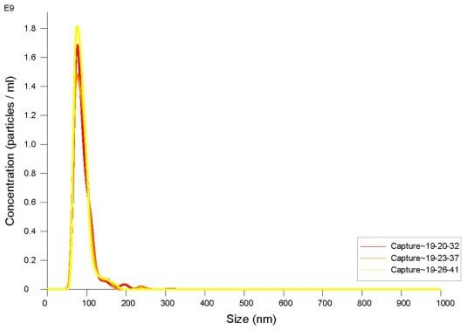


Figure S4. Freshly prepared samples of colloidal Ga-tpfc (top, right) and colloidal Al-tpfc (bottom, right) in 2% DMSO/water under fluorescent ambient light. The Ga sample (top, left) and the Al sample (bottom, left) under illumination (from bottom) with a white light source.

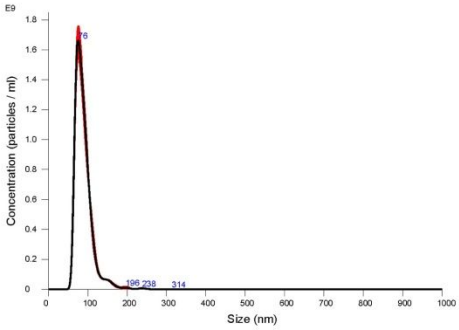
Note the blue-purple scattered light attributed to enhanced resonance scattering in the Soret band region.

NANOSIGHT

Au



FTLA Concentration / Size graph for Experiment:
Capture 2019-04-17 19-17-22



Averaged FTLA Concentration / Size for Experiment:
Capture 2019-04-17 19-17-22
Error bars indicate + / -1 standard error of the mean

Included Files

Capture 2019-04-17 19-20-32
Capture 2019-04-17 19-23-37
Capture 2019-04-17 19-26-41

Details

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Time Captured:	19:17:22 17/04/2019
Operator:	adb
Pre-treatment:	
Sample Name:	Au-tpfc 2 % DMSO 2nd run
Diluent:	
Remarks:	Au-tpfc 2% DMSO

Capture Settings

Camera Type:	sCMOS
Laser Type:	Blue488
Camera Level:	8
Slider Shutter:	317
Slider Gain:	15
FPS	25.0
Number of Frames:	4496
Temperature:	25.0 - 25.0 ºC
Viscosity:	(Water) 0.9 cP
Dilution factor:	1 x 10e2
Syringe Pump Speed:	15

Analysis Settings

Detect Threshold:	8
Blur Size:	Auto
Max Jump Distance:	Auto: 17.0 - 17.1 pix

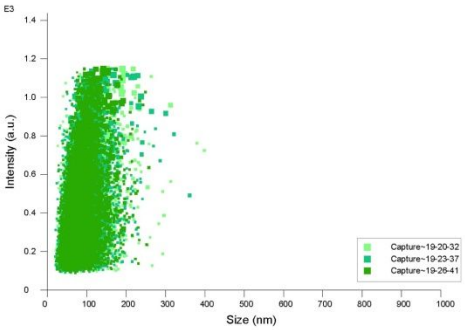
Results

Stats: Merged Data

Mean:	88.9 nm
Mode:	75.7 nm
SD:	22.8 nm
D10:	66.7 nm
D50:	83.2 nm
D90:	111.9 nm

Stats: Mean +/- Standard Error

Mean:	88.9 +/- 0.7 nm
Mode:	75.7 +/- 0.1 nm
SD:	22.7 +/- 1.4 nm
D10:	66.7 +/- 0.3 nm
D50:	83.2 +/- 0.4 nm
D90:	111.7 +/- 1.6 nm
Concentration (Upgrade):	6.36e+010 +/- 1.70e+009 particles/ml
	39.9 +/- 0.6 particles/frame
	41.0 +/- 0.7 centres/frame

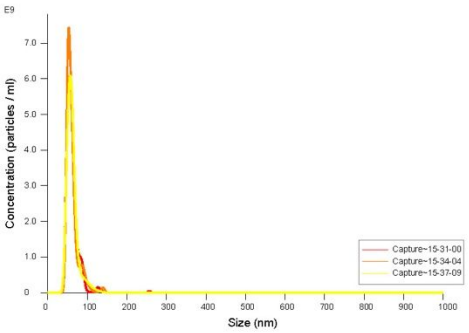


Intensity / Size graph for Experiment:
Capture 2019-04-17 19-17-22

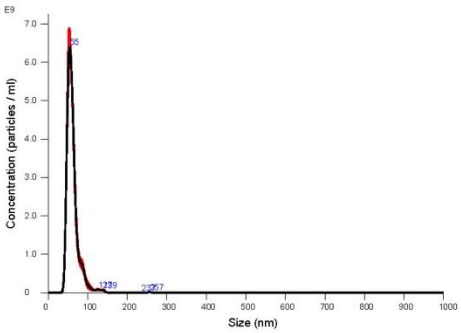
Figure S5.1 Complete list of experimental (left) and statistical (right) NTA parameters for Au-tpfc.

NANOSIGHT

Ga



FTLA Concentration / Size graph for Experiment:
Capture 2019-04-18 15-27-42



Averaged FTLA Concentration / Size for Experiment:
Capture 2019-04-18 15-27-42
Error bars indicate + / -1 standard error of the mean

Included Files

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Capture 2019-04-18 15-34-04
Capture 2019-04-18 15-37-09

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Operator:	adb
Pre-treatment:	
Sample Name:	Ga-tpfc 2 % DMSO DF = 200
Diluent:	
Remarks:	Ga-tpfc 2% DMSO DF 200 +24 hrs after mixing.

Capture Settings

Camera Type:	sCMOS
Laser Type:	Blue488
Camera Level:	10
Slider Shutter:	696
Slider Gain:	73
FPS	25.0
Number of Frames:	4496
Temperature:	25.0 - 25.0 °C
Viscosity:	(Water) 0.9 cP
Dilution factor:	2 x 10e2
Syringe Pump Speed:	15

Analysis Settings

Detect Threshold:	5
Blur Size:	Auto
Max Jump Distance:	Auto: 19.3 - 20.3 pix

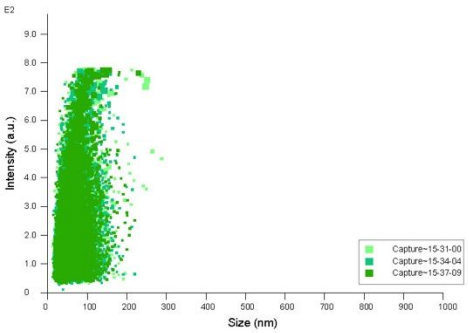
Results

Stats: Merged Data

Mean:	61.4 nm
Mode:	54.4 nm
SD:	16.0 nm
D10:	46.4 nm
D50:	57.0 nm
D90:	78.5 nm

Stats: Mean +/- Standard Error

Mean:	61.4 +/- 0.3 nm
Mode:	55.1 +/- 1.1 nm
SD:	16.0 +/- 0.8 nm
D10:	46.4 +/- 0.2 nm
D50:	57.0 +/- 0.6 nm
D90:	78.6 +/- 0.8 nm
Concentration (Upgrade):	1.54e+011 +/- 7.67e+008 particles/ml
	57.1 +/- 0.1 particles/frame
	57.1 +/- 0.1 centres/frame



Intensity / Size graph for Experiment:
Capture 2019-04-18 15-27-42

Figure S5.2 Complete list of experimental (left) and statistical (right) NTA parameters for Ga-tpfc.

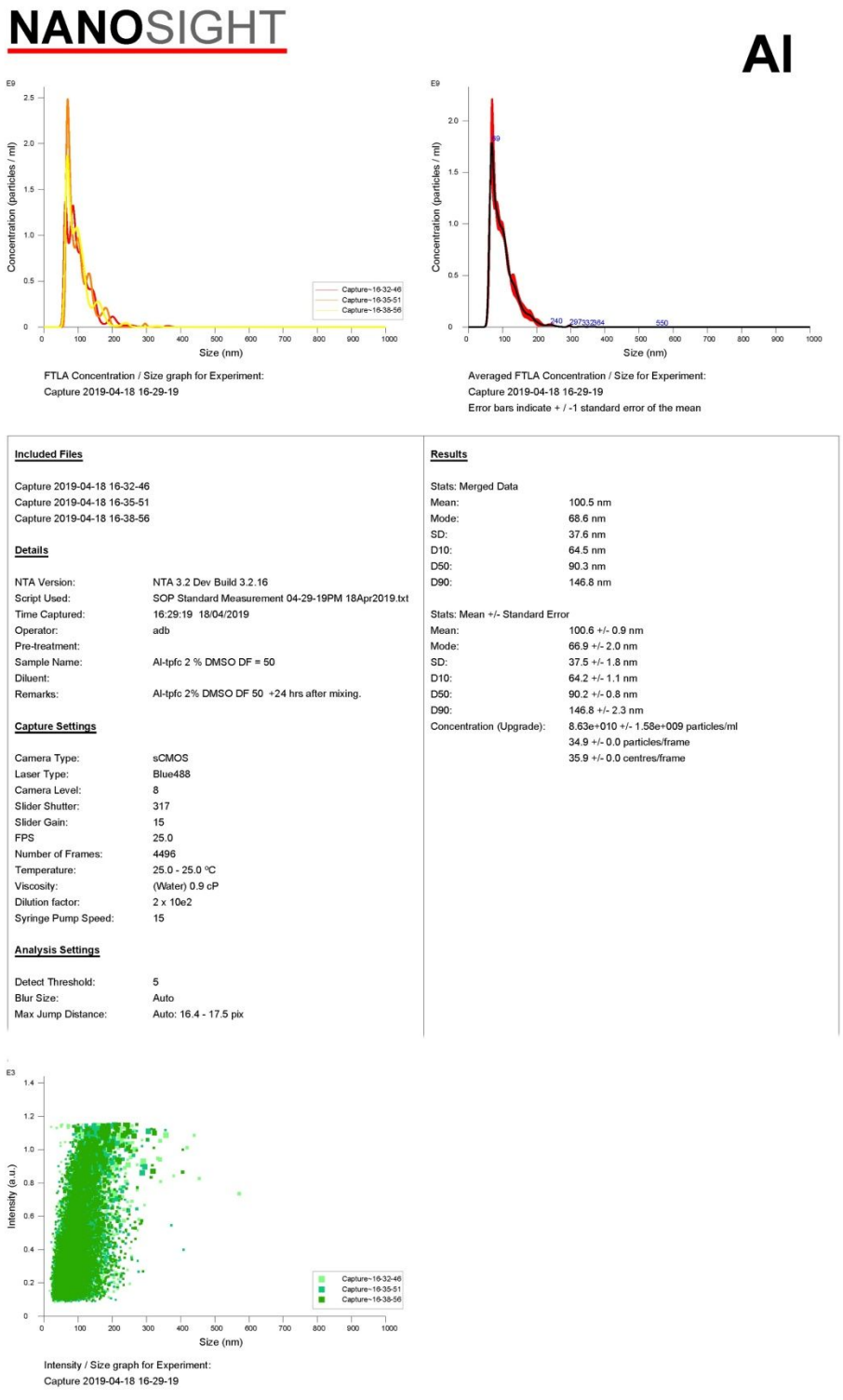


Figure S5.3 Complete list of experimental (left) and statistical (right) NTA parameters for Al-tpfc.

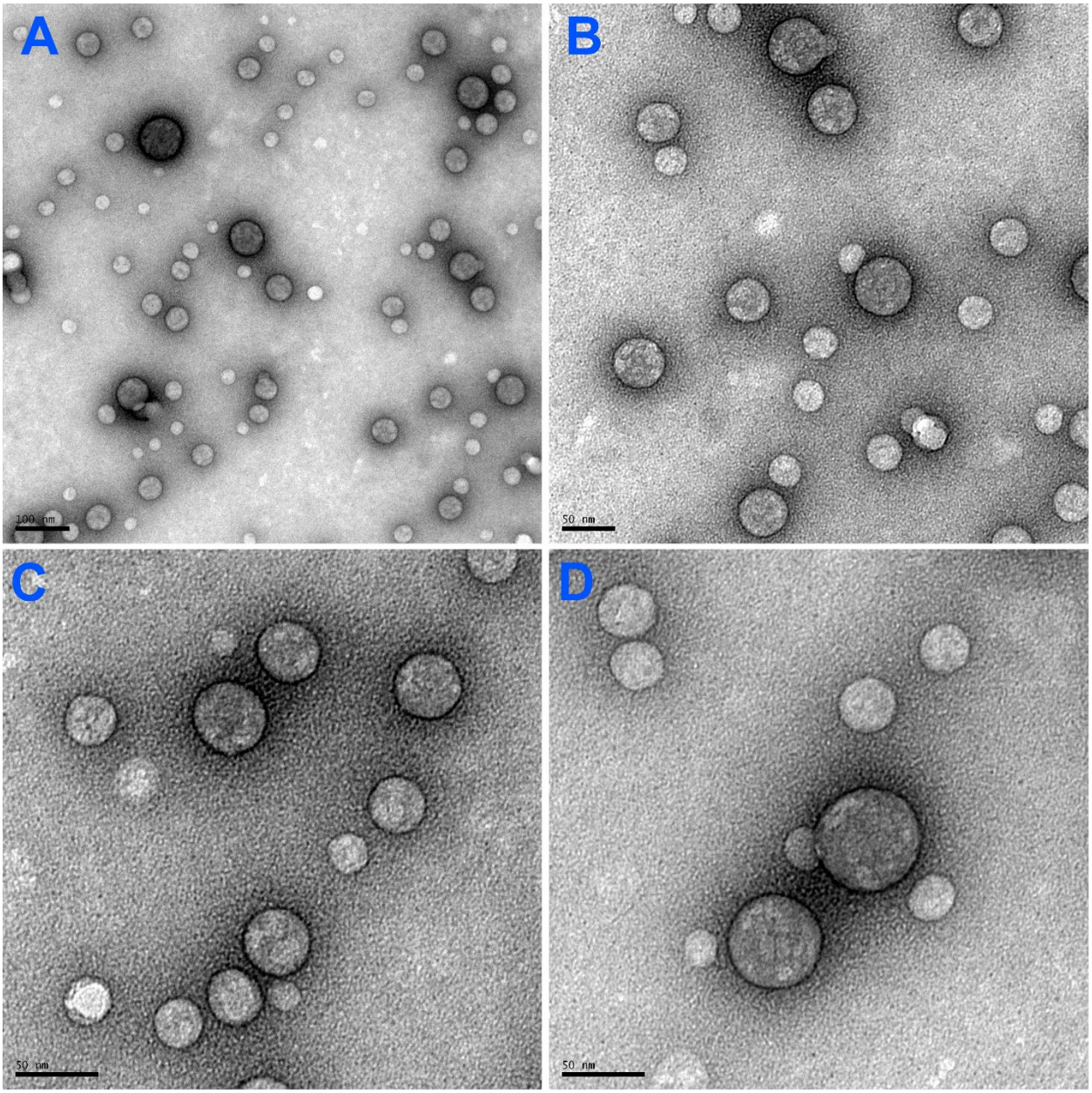


Figure S6. TEM images for Au-tpfc NPs prepared in 2% pyridine/water (room temperature). Panel A, 2.1 K magnification; panel B, 4.2 K magnification; panels C and D, 6.7 K magnification. Similar results were obtained for two different preparations. The images above were obtained from a sample, 24-hr-old. Images from a 3-week old sample were similar.

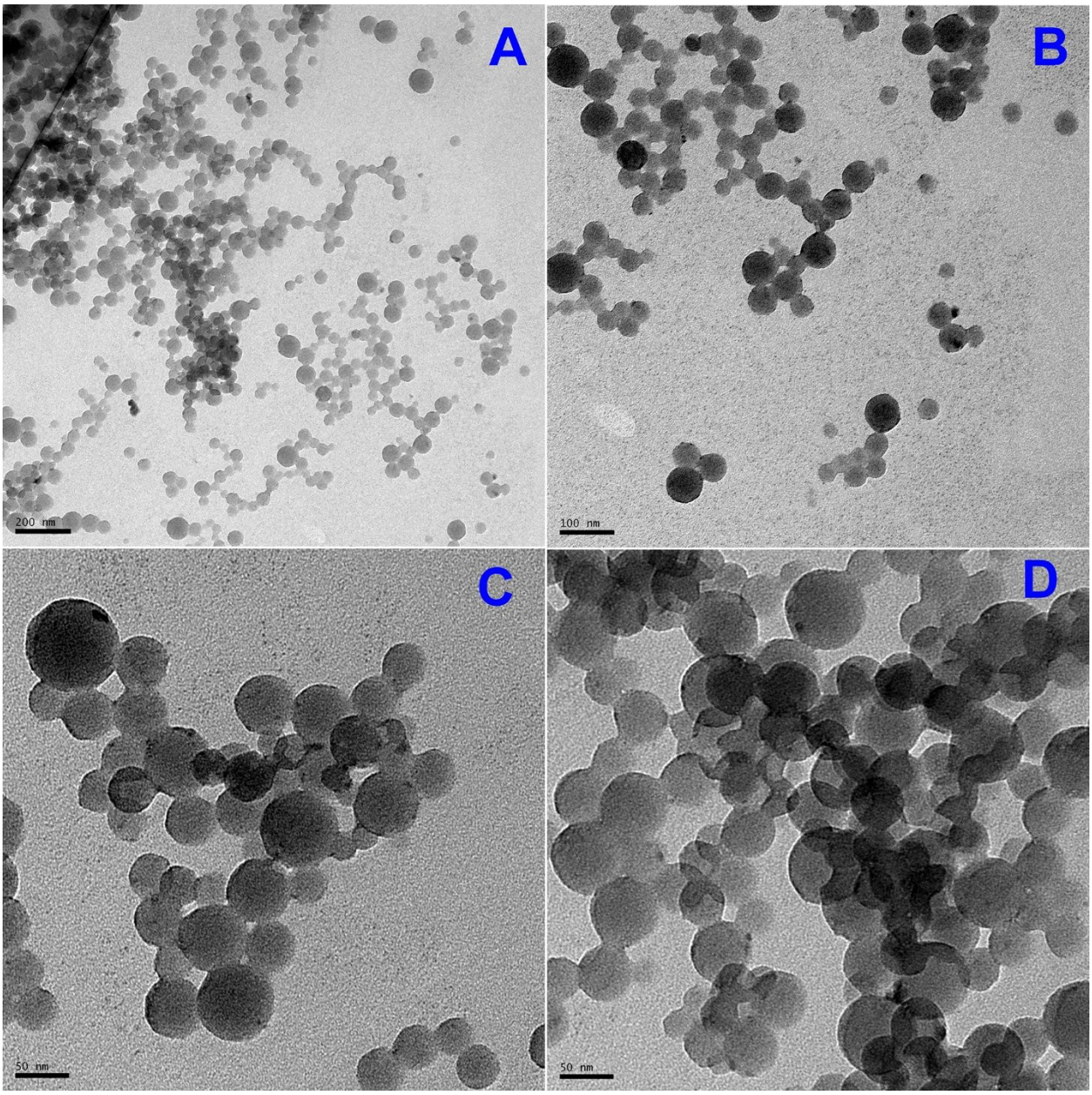


Figure S7. TEM images for Ga-tpfc NPs prepared in 2% pyridine/water (room temperature). Panel A, 1.1 K magnification; panel B, 2.1 K magnification; panels C and D, 4.2 K magnification. The images above were obtained from a sample, 24-hr-old. Images from a 3-week old sample were similar.

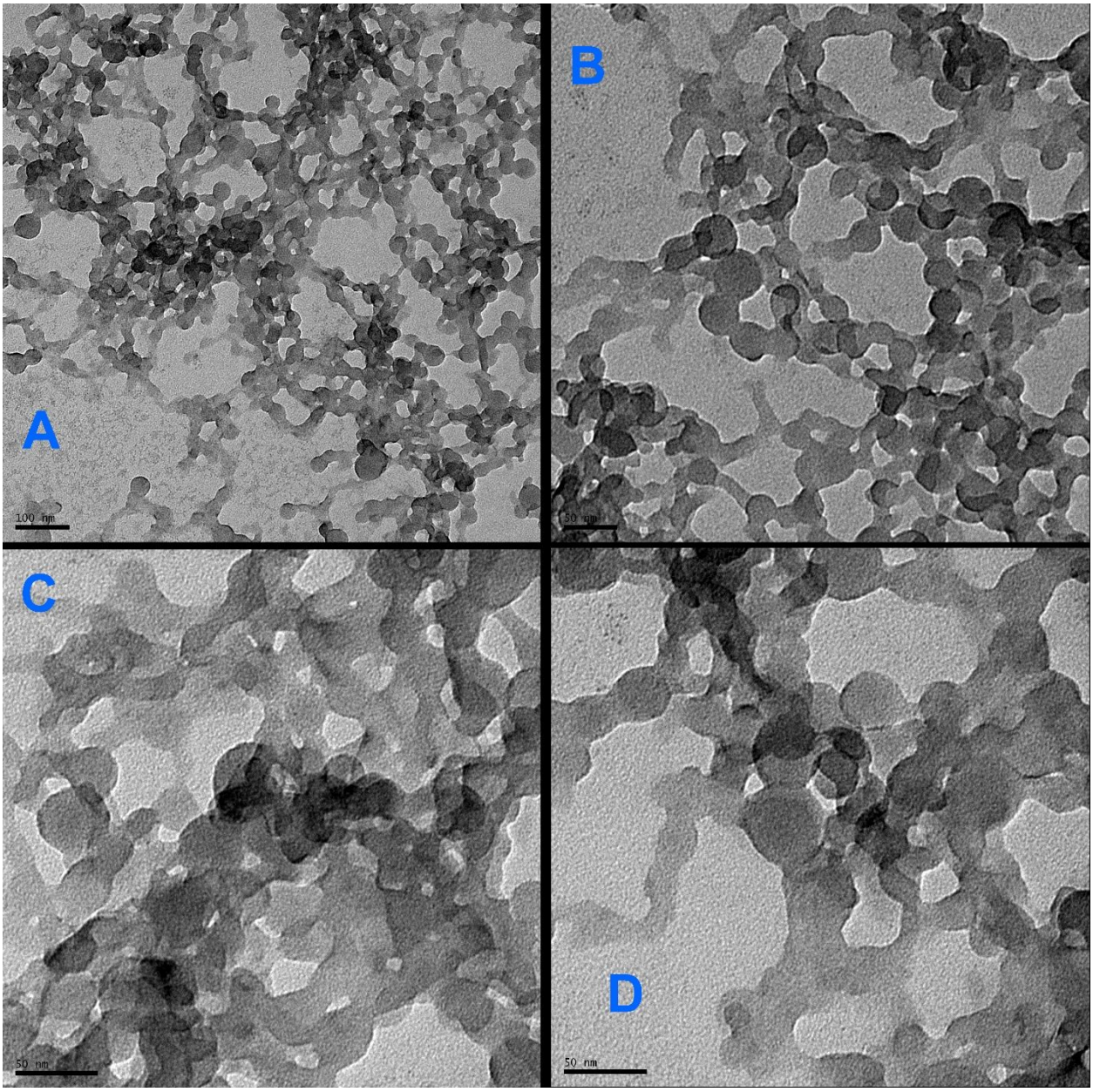


Figure S8. TEM images for Al-tpfc NPs prepared in 2% pyridine/water (room temperature). Panel A, 2.1 K magnification; panel B, 4.2 K magnification; panels C and D, 6.7 K magnification. The images were obtained from a 24-hr-old sample.

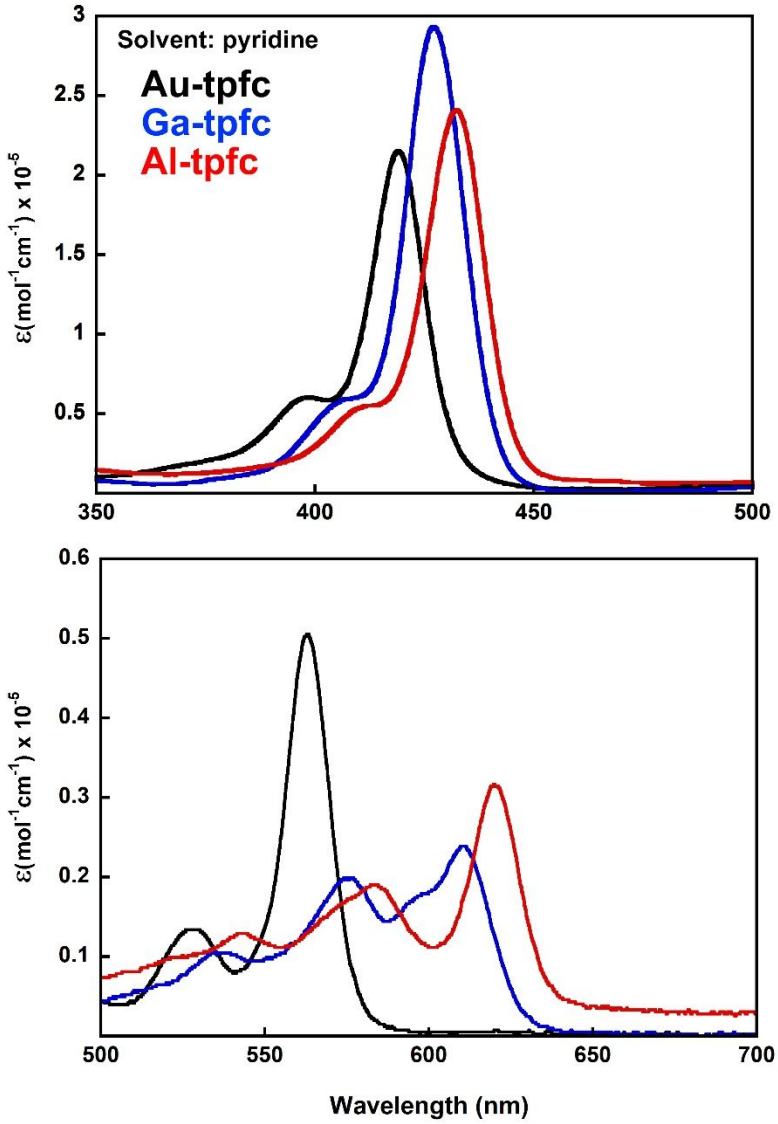


Figure S9. (Top and bottom) UV-visible absorption spectra in pure pyridine [λ_{max} (nm); ε $mol^{-1}cm^{-1}$ for Au-tpfc [419.0; 2.15 x 10^5]; Ga-tpfc-py [427.2; 2.46 x 10^5]; and Al-tpfc-py_2 [432.2; 2.41x 10^5].

UV-visible absorption spectral data in pure DMSO [λ_{max} (nm); ε $mol^{-1}cm^{-1}$ for Au-tpfc [416; 2.18 x 10^5]; Ga-tpfc-py [420; 2.63 x 10^5]; and Al-tpfc-$(py)_2$ [432; 1.83 x 10^5].

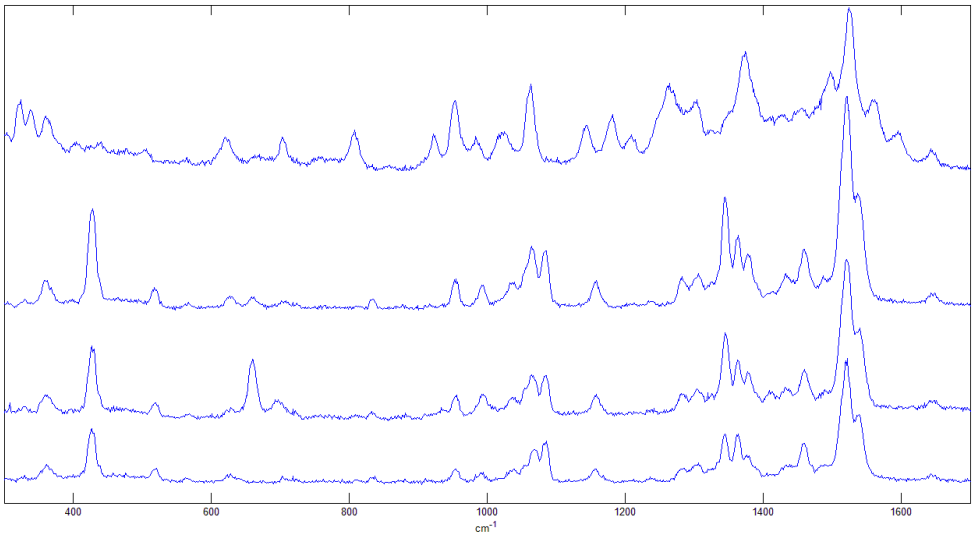


Figure S10. Raman spectra (top to bottom): tpfc NPs in 2% DMSO; Au-tpfc NPs in 2% DMSO gel; Au-tpfc NPs in 5% DMSO; Au-tpfc crystal; 457.9 nm excitation.

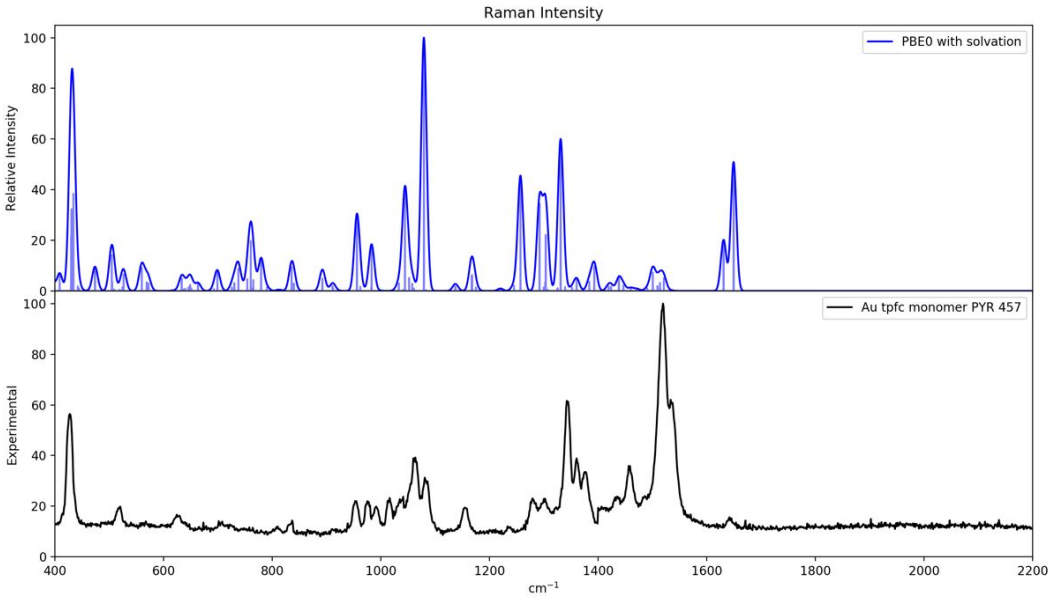


Figure S11. (Top) Raman spectrum of Au-tpfc calculated using PBE0/LACV3P** with a 0.96 vibrational shift and gaussian smoothing (standard deviation of 5 cm^{-1}). (Bottom) Experimental Raman spectrum of Au-tpfc in pyridine; 457.9 nm excitation.

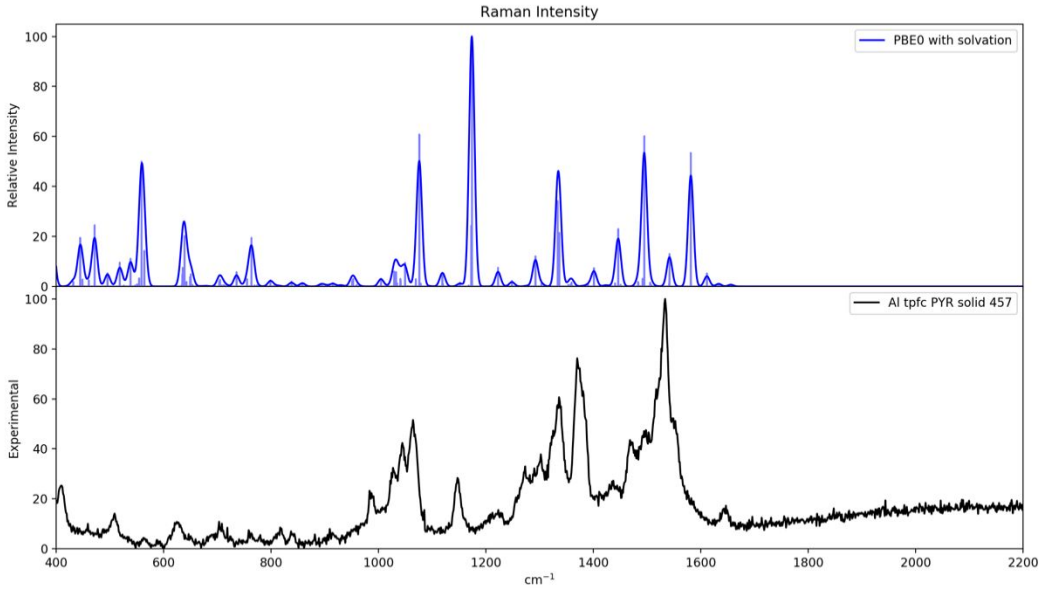


Figure S12. (Top) Raman spectrum of Al-tpfc with 2 axial pyridines calculated using PBE0/6-31G with a 0.96 vibrational shift and gaussian smoothing (standard deviation of 5 cm^{-1}). (Bottom) Experimental Raman spectrum of Al-tpfc in pyridine; 457.9 nm excitation.

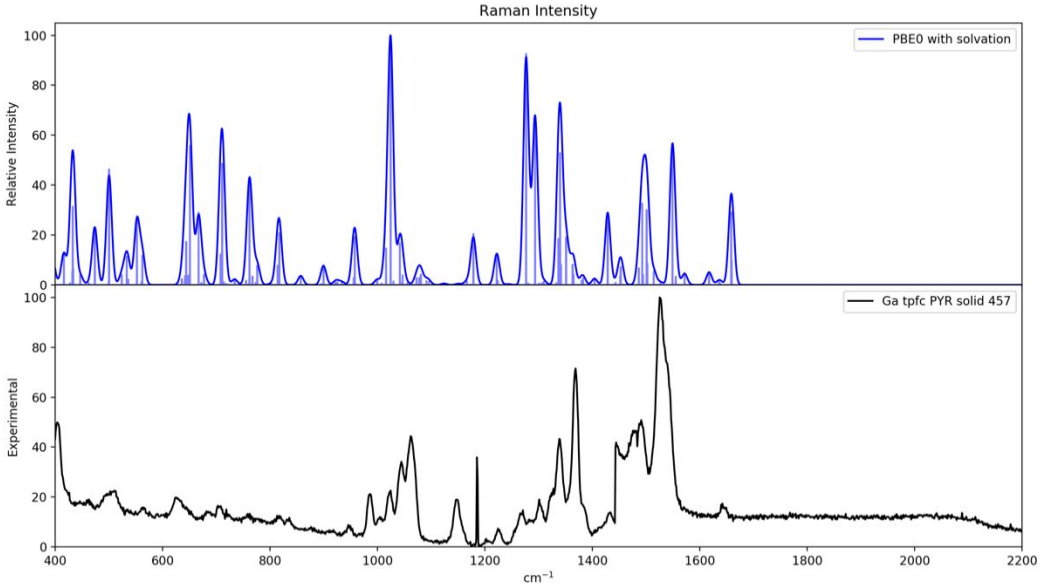


Figure S13. (Top) Raman spectrum of Ga-tpfc with 1 axial pyridine calculated using PBE0/6-31G with a 0.96 vibrational shift and gaussian smoothing (standard deviation of 5 cm^{-1}). (Bottom) Experimental Raman spectrum of Ga-tpfc in pyridine; 457.9 nm excitation.

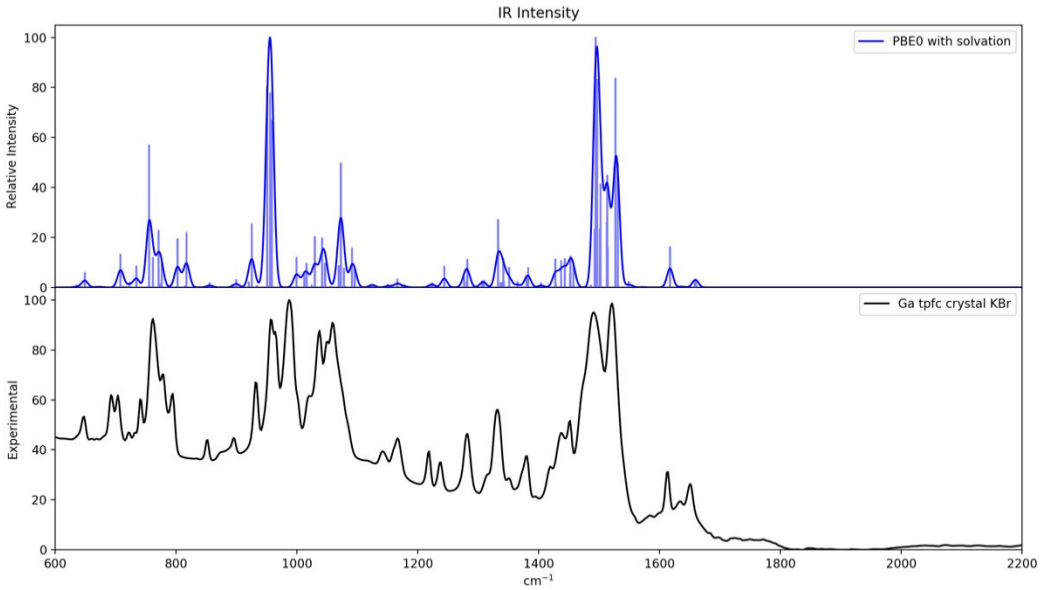


Figure S14. (Top) IR spectrum of Ga-tpfc with 1 axial pyridine calculated using PBE0/6-31G

with a 0.96 vibrational shift and gaussian smoothing (standard deviation of 5 cm^{-1}). (Bottom) Experimental IR spectrum of crystalline Ga-tpfc.

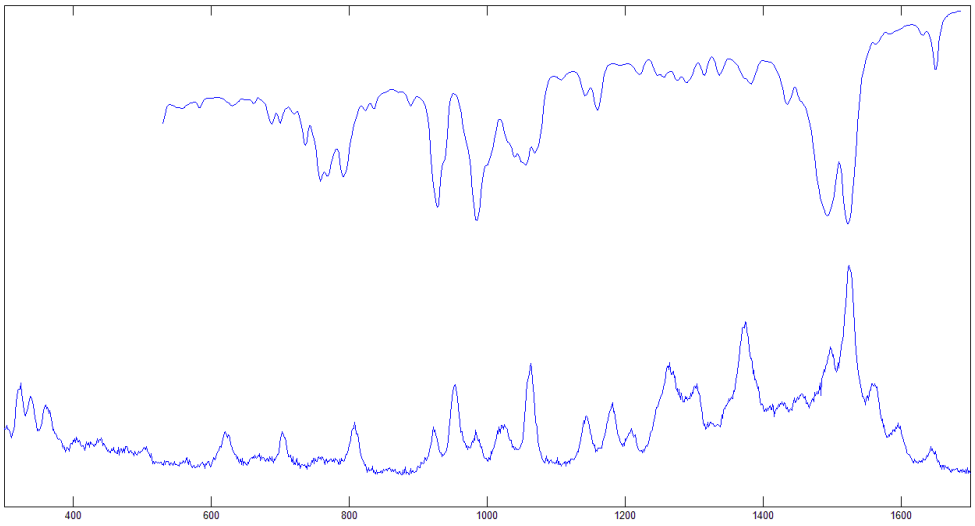


Figure S15. (Top) IR spectrum of free base tpfc; (Bottom) Raman spectrum of free base tpfc NPs in 2% DMSO; 457.9 nm excitation.

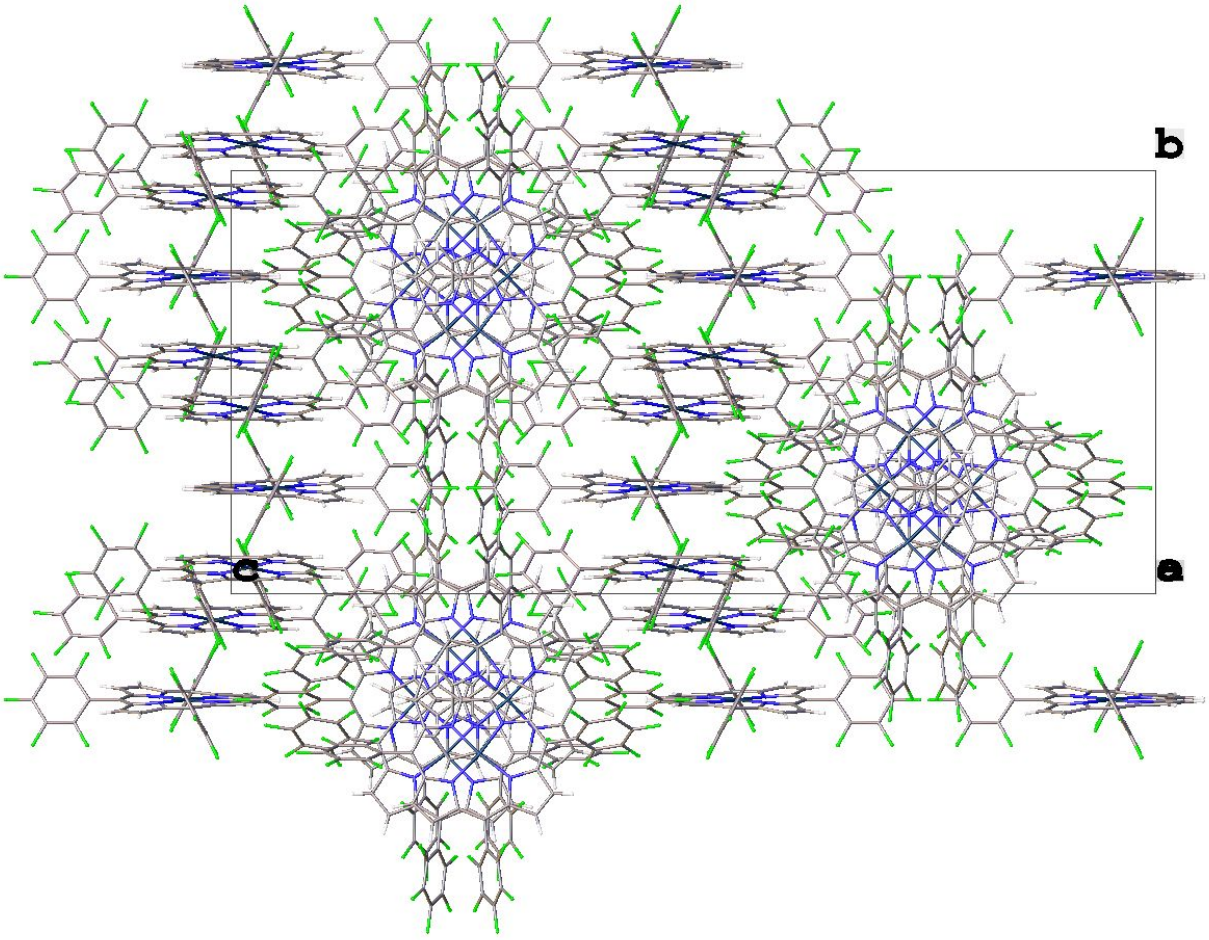
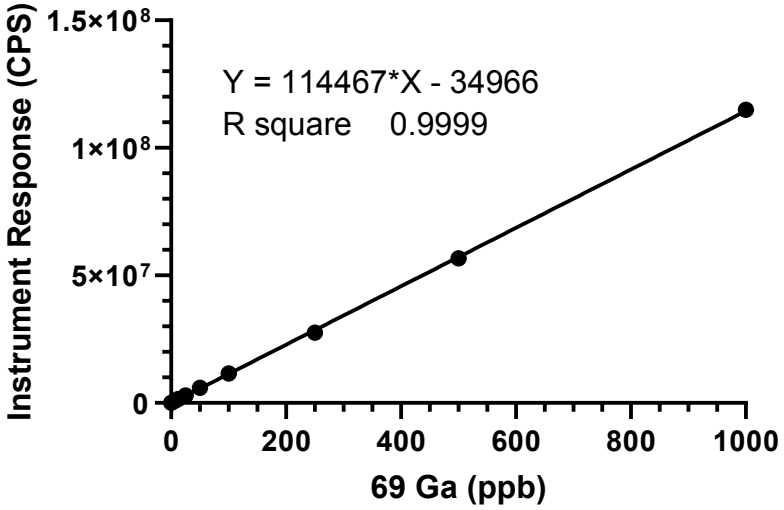


Figure S16. View of corrole packing in a Au-tpfc crystal. Crystallographic data (CCDC 1914233) can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/structures.

ICP-MS. A stock solution of 2% HNO_3, 1% HCl solution was made by adding 28 mL HNO_3 (70%) and 27 mL HCl (37%) to 945 mL mQ H_2O and stored in a plastic bottle. A stock solution of concentrated acid (68% HNO_3, 1% HCl) was made fresh by adding 0.27 mL HCl (37%) to every 10 mL HNO_3 (70%). 2.5, 5, or 15 μL of concentrated metallocorrole NPs in 2% DMSO/water or pyridine/water were added to a 15 mL metal free tube (SCP Science), representing three replicates for each metallocorrole NP. 500 μL concentrated acid (68% HNO_3, 1% HCl) were added into each tube and allowed to digest at 80ºC for a minimum of 15 min. 4.5 mL of the 2% HNO_3, 1% HCl mQ solution were then added to each tube. A 1000 ppb (1 μg mL^{-1}) standard containing gold was made by adding 150 μL of a 100 ppm (100 μg mL^{-1}) gold standard (Spex CertiPrep) to 14.85 mL of 2% HNO_3, 1% HCl mQ solution. A 1000 ppb gallium calibration standard solution was purchased from Spex CertiPrep. The 1000 ppb standard of gold or gallium was then serially diluted using the 2% HNO_3, 1% HCl mQ solution to make a standard curve ranging from 1.95 to1000 ppb. Samples were analyzed on an Agilent 8800 ISIS (discrete sampling) in no gas mode to determine gold or gallium concentrations. The 2% HNO_3, 1% HCl solution in mQ water was used for both rinse and carrier solutions. Each sample was measured 5 times (technical replicates). A blank solution/calibration standard was measured after approximately every 10 samples as quality control to ensure that there was no carry-over between samples, and to check for instrument stability. The total amount of gold or gallium in 2.5, 5, or 15 μL of each concentrated metallocorrole NP sample was calculated by multiplying the measured concentration (ppb) with the 5 mL total volume of sample after dilution. Measurements below the lower limit of the standard curve were considered to be zero.

a)



b)

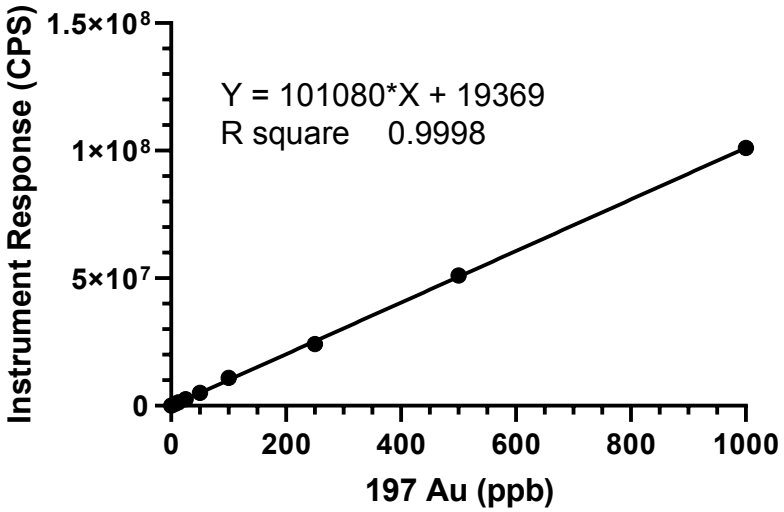


Figure S17. Calibration curves for gallium (a) and gold (b) standards over a concentration range of 1.95 to 1000 ppb.

Table S1. Hydrodynamic diameters measured by DLS and NTA and concentrations (measured by NTA) summary.

Metal-corrole NP		**Hydrodynamic diameter (nm)**		**Concentration (particle mL^{-1})**
Solv.	**NP**	**DLS; Nanosight**	**PDI**	
2% DMSO	Au-tpfc	89; 83	0.121	6.36×10^{10}
	Ga-tpfc	66; 57	0.097	15.4×10^{10}
	Al-tpfc	128; 90	0.319	8.63×10^{10}
2% pyridine	Au-tpfc	91; 71	0.065	4.84×10^{10}
	Ga-tpfc	78; 67	0.07	25.2×10^{10}

Table S2. Calculations and equations used to determine metal-corrole per particle for each metal-corrole NPs using paired NTA and ICP-MS analysis.

Samples	Nanoparticle Tracking Analysis (NTA)				ICP-MS					
	Median (nm)	SD (nm)	[Particle] ($x10^8$/mL)	±Particle SE ($x10^8$/mL)	Au (ppm)	±Au SD (ppm)	Au/mL (mol)	Au/mL (molecules)	Au ($particle^{-1}$)	**Au ($x10^5$/particle)**
AuNP/2% DMSO	83	23	636	17	8.975	1.214	4.56E-08	2.74E+16	431365.9	**4.3**
AuNP/2% Pyridine	72	15	484	103	10.836	0.581	5.50E-08	3.31E+16	684351.8	**6.8**

Samples	Nanoparticle Tracking Analysis (NTA)				ICP-MS					
	Median (nm)	SD (nm)	[Particle] ($x10^8$/mL)	±Particle SE ($x10^8$/mL)	Ga (ppm)	±Ga SD (ppm)	Ga/mL (mol)	Ga/mL (molecules)	Ga ($particle^{-1}$)	**Ga ($x10^5$/particle)**
GaNP/2% DMSO	57	16	1540	8	5.528	0.034	8.01E-08	4.82E+16	313303.4	**3.1**
GaNP/2% Pyridine	67	12	2520	25.1	6.107	0.197	8.85E-08	5.33E+16	211516.8	**2.1**

$$\text{mole of M / mL} = \frac{\text{(ppm of M)}}{\text{(MW of M x 0.000001)}}$$

$$\text{M} = \text{gallium (Ga) or gold (Au)}$$

$$\text{MW of Ga} = 69$$

$$\text{MW of Au} = 197$$

$$1 \text{ ppm} = 1 \text{ μg / mL}$$

$$\text{M / particle} = \frac{\text{(molecule of M / mL)}}{\text{(particles / mL)}}$$

$$\text{molecule of M / mL} = \text{(mole of M)} \times (6.022 \times 10^{23})$$

Table S3*:* Free energies (kcal/mol) associated with axial ligand binding to Ga-tpfc. All structures optimized with PBE-D3/LACV3P**++.

	Free Energy (kcal/mol)	Ga-L Bond (Å)
DMSO (O-bound)	-41.4	1.99
DMSO (S-bound)	-8.7	2.82
H_2O	-28.8	2.05
Pyridine	-35.9	2.10

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